

PCT

THE BRITISH LIBRARY
SCIENCE REFERENCE AND INFORMATION S
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03D 13/00		A2	(11) International Publication Number: WO 96/14274
			(43) International Publication Date: 17 May 1996 (17.05.96)
(21) International Application Number: PCT/EP95/04394		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).	
(22) International Filing Date: 8 November 1995 (08.11.95)			
(30) Priority Data:			
9422468.0 8 November 1994 (08.11.94) GB			
9424126.2 23 November 1994 (23.11.94) GB			
9424127.2 23 November 1994 (23.11.94) GB			
9500667.2 13 January 1995 (13.01.95) GB			
(71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S [DK/DK]; Hovedgaden 501, DK-2640 Hedehusene (DK).		Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(72) Inventors; and			
(75) Inventors/Applicants (for US only): JENSEN, Soren, Lund [DK/DK]; Tordenskjoldsgade 23, 2 th., DK-1055 Kobenhavn (DK). CHRISTENSEN, Vermund, Rust [DK/DK]; Soager 11, DK-4000 Roskilde (DK). GULDBERG, Marianne [DK/DK]; Niels Finsens Alle 5, DK-2860 Soborg (DK).			
(74) Agent: JONES, Helen; Gill Jennings & Every, Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).			

(54) Title: MAN-MADE VITREOUS FIBRES

(57) Abstract

Man-made vitreous fibres have a solubility at pH 4.5 of at least 20 nm per day and a melt viscosity of 10-70 poise at 1,400 °C. A composition which will provide these properties is selected for their manufacture and contains at least 10 % by weight Al₂O₃. Novel fibres contain at least 6 % by weight Na₂O + K₂O.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Man-Made Vitrous Fibres

This invention relates to man-made vitreous fibres (MMVF) which are durable in use but which can be shown to
5 be biologically advantageous.

MMV fibres are made from vitreous melt, such as of rock, slag, glass or other mineral melts. The melt is formed by melting in a furnace a mineral composition having the desired analysis. This composition is generally
10 formed by blending rocks or minerals to give the desired analysis. The mineral composition often has an analysis, as oxides, which includes at least 32% SiO₂, below 30% Al₂O₃ and at least 10% CaO. The elemental analyses in the specification are by weight and calculated as oxides. The
15 iron oxide may be a mixture of FeO and Fe₂O₃, but is quoted herein as FeO.

Efficient and cost-effective formation of the melt in the furnace and of the fibres from the melt requires that the composition should have a suitable liquidus temperature
20 and should have a suitable viscosity during the fibre-forming process. These requirements impose constraints on the selection of the composition that is to be melted.

Although there is no scientific evidence establishing that there is a health risk associated with the manufacture
25 and use of MMV fibres, commercial interests have led manufacturers to provide MMV fibres that retain the required physical properties of MMV fibres (e.g., durability at elevated temperatures and under humid conditions) but which can also be alleged to be of improved
30 biological safety.

This allegation of improved safety is usually made on the basis of an in vitro test that examines the dissolution rate or degradability of the fibres in a liquid which is intended to simulate lung liquid, such as Gamble's solution
35 with pH 7.4 to 7.8. A consequence of enhanced dissolution rate at pH 7.5 is that the fibres will normally have reduced resistance to humidity.

Numerous patent applications have been published describing fibres that give enhanced dissolution rate in such an in vitro test, such as WO87/05007, WO89/12032, EP 412878, EP459897, WO92/09536, WO93/22251 and WO94/14717.

5 A characteristic of many of these patent applications, and of fibres which are alleged to have enhanced dissolution rate in such in vitro tests, is that the fibre should have reduced aluminium content. For instance it is stated in WO87/05007 that the Al_2O_3 amount must be below 10%. The aluminium content of rock wool and slag wool is generally in the range 5 to 15% (measured as Al_2O_3 by weight) and many of these allegedly biologically suitable fibres have an aluminium content of below 4%, and often below 2%. It is known to include phosphorous in these 15 low- Al_2O_3 compositions in order to increase the dissolution rate in this pH 7.5 dissolution rate test.

A problem with many of these low- Al_2O_3 fibres (in addition to uncertainty as to whether they do have enhanced biological suitability) is that the melt properties are not 20 entirely satisfactory for manufacture in conventional or easily adapted melting and fibre-forming apparatus. For instance the melt viscosity at convenient fibre-forming temperatures may be rather low. Another problem is that a high dissolution rate at pH 7.5 may tend to result in 25 reduced durability under humid conditions which may be experienced after installation.

In addition to the in vitro tests, in vivo research testing has been conducted. For instance Oberdörster in VDI Berichte 853, 1991, pages 17 to 37 showed that two 30 basic mechanisms are involved in the clearance of fibres from the lungs, namely dissolution in the near-neutral lung fluid and dissolution in the acidic environment (maintained at pH 4.5 to 5) created around fibres surrounded by macrophages in the lung. It is believed macrophages 35 promote removal of the fibres from the lung by promoting local dissolution of the surrounded fibre area leading to weakening and breaking of the fibres so as to reduce the

average fibre length, thereby enabling macrophages to engulf and transport the shorter fibres out of the lung. This mechanism is illustrated in the article by Morimoto et al in Occup. Environ. Med 1994, 51, 62-67 and especially 5 Figures 3 and 7 and articles by Luoto et al in Environmental Research 66 (1994) 198-207 and Staub-Reinhaltung der Luft 52 (1992) 419-423.

Traditional glass fibres and many of the MMV fibres claimed to have increased solubility in lung fluid (at pH 10 7.5) have a worse solubility at pH 4.5 than at pH 7.5 and so presumably attack by macrophages would not contribute significantly to the shortening and final removal of the fibres from the lung.

Existing MMV fibres formed from rock, slag and other 15 relatively high alkaline earth mixtures can have a higher dissolution rate at pH 4.5 than pH 7.5 but tend to have a low melt viscosity. Existing fibres which are promoted as being biologically acceptable do not have a satisfactory 20 combination of dissolution rate at pH 4.5 with melt properties. Fibres which are currently alleged to be preferred on the basis of in vitro tests tend to have low melt viscosity when they have the required low aluminium content. The low melt viscosity inevitably reduces production efficiency compared to normal production.

It would be desirable to provide MMV fibres which can 25 be shown to be biodegradable in the lung, have melt properties which allow for normal, high, production efficiency and which can be made from inexpensive raw materials. Preferably they have good weathering resistance 30 when exposed to ambient humid conditions in use.

In the invention we use, as fibres having satisfactory biological solubility, fibres which have a dissolution rate measured at pH 4 to 5 of at least 20nm per day and which 35 are formed of a composition having a melt viscosity at 1,400°C of 10-70 poise. For instance the dissolution rate at pH 4.5 can be at least 30 or even at least 50 nm per day or more.

The combination of the melt viscosity and the solubility at pH 4.5 means that we can use a melt which is convenient to fibreise by conventional techniques and can produce fibres which are biologically soluble at pH 4.5.

5 It is new to formulate or select fibres according to this combination, and many such fibres have a novel composition.

In a preferred aspect of the invention we determine the melt viscosity and the fibre dissolution rate at a pH in the range 4-5 of one or more compositions, we select a 10 composition which has a melt viscosity at 1400°C of 10 to 70 poise and provides fibres which have a dissolution rate at pH 4.5 of at least 20nm per day and which has an analysis, measured as weight of oxides, which includes

	SiO ₂	32 to 48%
15	Al ₂ O ₃	10 to 30%
	CaO	10 to 30%
	MgO	2 to 20%
	FeO	2 to 15%
	Na ₂ O + K ₂ O	0 to 12%
20	TiO ₂	0 to 6%
	Other Elements	0 to 15%

and we make fibres from this composition.

It is surprisingly possible, in accordance with the invention, to provide fibres which have a good dissolution 25 rate at pH 4.5 thereby facilitating clearance from the lungs by macrophages (thus promoting genuine biodegradability), even though the fibres can have low or moderate dissolution rate at pH 7.5. This allows maintenance of good stability under humid conditions 30 (without loss of biodegradability). The fibres can have reasonably conventional melt characteristics such as liquidus temperature, crystallisation rate and melt viscosity. The fibres can be formed using inexpensive raw materials.

35 Another advantage of the fibres is that when they are exposed to humidity and condensed water, the resultant solution that is formed containing dissolution products has

increased pH but the fibres may have reduced solubility at increased pH and so they may dissolve less and have increased durability.

The invention broadly includes all MMVF products made from a composition having the melt viscosity at 1,400°C of 10-70 poise and wherein the manufacture, promotion or sale or use involves measurement of, or reference to measurement of, solubility at about pH 4.5 (e.g., 4 to 5) and/or in the environment of macrophages in the lung irrespective of whether the dissolution rate is measured during the actual production of such products. The fibres preferably have an analysis as stated above.

The invention includes the use of the stated composition to promote the removal of MMVF fibres from human lungs. The invention also includes the use of the stated fibres to impart the ability to be rejected from human lungs.

The invention includes MMVF products, including MMV fibres, made from a composition which has been selected in order to provide the stated solubility. For instance it includes the measurement of pH 4-5 solubility and the melt viscosity of one or more compositions and selecting a composition partly or wholly on the basis of observing melt viscosity and solubility value at pH 4-5, and utilising compositions having the same or substantially the same analysis for making MMVF products. Any deviations in the analysis must be sufficiently small that they do not significantly alter the pH 4-5 solubility. When conducting the measurements to allow a selection of fibres to be made, the solubility can be determined at any pH (usually in the range 4-5) which correlates to the pH at 4.5. The melt viscosity can be determined either by deduction from data or by measurement and/or calculation, for any temperature (usually in the range 1,370-1,450°C) which gives a value which correlates with the value at 1,400°C.

The selection of the composition does not have to be conducted at the same location or at about the same time as

carrying out the commercial production using the selected composition. Thus a manufacturer may conduct tests, or sponsor others to conduct tests, to determine solubility and use the information from these tests as part of the 5 basis for selecting the composition which is used for making the fibres commercially.

The invention includes products having the quoted analysis and are formed from a composition having the quoted melt viscosity and which are labelled or sold as 10 having the defined dissolution rate at pH 4-5. The invention includes packages which contain MMVF fibres and which carry a label or insert, or which are sold with advertising, which refers to solubility at pH in the range 4-5 or in the environment of macrophages or which refers to 15 a test method which measures such solubility.

The invention includes novel MVVF products. These include horticultural MMVF growth media and fibre reinforcement wherein the fibres are as defined in the invention.

One class of fibres which are novel are fibres having 20 the solubility, melt viscosity and composition analysis given above except that the amount of Al_2O_3 is at least 18%. Other useful fibres have Al_2O_3 above 16%. Often it is above 25 19 or 20%, for instance up to 26 or 28%. In fibres having Al_2O_3 above 16% the combined amount of alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) is usually at least 1% and preferably at least 2%, up to 7% or 10% or more. The amount of alkali is usually below 5% and 30 preferably below 3% when the amount of Al_2O_3 is above 16%. These fibres can have good fire resistance and other mechanical properties. When these properties are of less importance, fibres having useful pH 4.5 solubility can be obtained with amounts of Al_2O_3 below 16% and amounts of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ above 6 or 7%, for instance 8 to 12%, usually 8-35 10%.

Another class of fibres which are novel are fibres which preferably have the solubility and melt viscosity given above and which have the general analysis given above

except that the alkali ($\text{Na}_2\text{O}+\text{K}_2\text{O}$) is above 6% and the amount of Al_2O_3 is usually 12-18%, and is often not more than 16% preferably 13-16%. Often the composition contains 0.5-4% TiO_2 , usually 1-2% TiO_2 . The alkali is usually provided by 5 at least 5% and often at least 7%, Na_2O . The total amount of alkali ($\text{Na}_2\text{O}+\text{K}_2\text{O}$) is preferably 8-12%, often 8-10%.

It is possible to select elemental analyses within the general ranges given above so as to obtain the defined combination of melt viscosity and dissolution rate at pH 10 4.5. Also, it is easily possible to select the composition such that the composition and the fibres comply with other desirable properties, such as liquidus temperature and sintering temperature.

For instance, if it is found that the viscosity at 15 1400°C of any particular melt is too high, it may be possible to reduce it by reducing the total amount of SiO_2 + Al_2O_3 . Similarly, if the melt viscosity is too low, it may be possible to increase it by raising the total amount of SiO_2 + Al_2O_3 , generally within the range of 55 to 75%, 20 often 60 to 75%, or by increasing the amount of alkali oxide. Similarly, it may be possible to decrease the viscosity by increasing the total amount of alkaline earth metal oxide components and FeO .

If the rate of dissolution at pH 4.5 is too low it may 25 be possible to increase it by decreasing the amount of SiO_2 , but it may then be necessary to increase the amount of Al_2O_3 (and/or to add a component such as P_2O_5) in order to maintain melt properties.

The amount of SiO_2 is normally at least 32%, often at 30 least 34% and preferably at least 35%. It is normally below 47% and preferably below 45% and is often 38-42%. However amounts of 42 to 47% are preferred when the amount of Al_2O_3 is not more than 16%.

The amount of Al_2O_3 is normally at least 12% and 35 preferably at least 13%. When the amount of alkali is relatively low, good solubility at pH 4.5 can be obtained with Al_2O_3 amounts above 16 or 17%, especially at least 18%,

but preferably at least 20% and often at least 24%. It is normally below 28% and preferably below 26%. Amounts of 20-23% are often preferred. However when the amount of alkali is relatively high (for instance at least 7% Na₂O+K₂O) good solubility at pH 4.5 can be obtained with Al₂O₃ amounts below 16%, eg 13-15%.

The combined amount of SiO₂ + Al₂O₃ is normally 55 to 75%, usually at least 56% and preferably at least 57%. In preferred products it is often above 60%, most preferably at least 61 or 62%. It is normally below 70% or 68% and preferably below 65%. When the amount of Al₂O₃ is not more than 16%, the amount of SiO₂+Al₂O₃ is often 56-60%.

The amount of CaO is normally at least 14% and preferably at least 18%. It is normally below 28% and preferably below 25%. Amounts of 14-20% are often preferred.

The amount of MgO is normally at least 5%, preferably at least 6% and most preferably at least 8%. It is normally below 15%, preferably below 11%. When the amount of Al₂O₃ is not more than 16%, the amount is preferably 5-11%.

The amount of FeO is normally at least 3% and preferably at least 5%. It is normally below 12%, preferably below 10% and most preferably below 8%. Amounts of 5-7% are often preferred. Preferably CaO + MgO + FeO is 25 to 40%.

The composition often includes TiO₂ in an amount of up to 3% or 4%, usually up to 2%. The amount of TiO₂ is usually at least 0.2%, often at least 0.5 or 1%.

A variety of other elements can be present in the composition in any amount that does not detract from the desired properties Examples of other elements that can be included are P₂O₅, B₂O₃, BaO, ZrO₂, MnO, ZnO and V₂O₅.

It is often desirable to include P₂O₅ and/or B₂O₃ for instance to adjust melt properties or to adjust solubility. The total amount of P₂O₅ and B₂O₃ is generally not more than 10%. The amount of P₂O₅ is usually more than the amount of

B_2O_3 and is usually at least 1% or 2%. Often B_2O_3 is absent. Preferably there is 1 to 8%, usually 1 to 5%, P_2O_5 and 0 to 5% B_2O_3 (often 1 to 4% B_2O_3).

5 The total amount of these various other elements is usually below 15% and often below 10% or 8%. Each of the other elements which is present is normally present in an amount of not more than 2%, except than P_2O_5 and/or B_2O_3 may be present in larger amounts as mentioned above.

10 The melt can have normal crystallisation characteristics, but when it is desired to minimise crystallisation this can be achieved by including magnesium in a rather low amount for instance 2 to 6% MgO.

15 When it is desired to provide fibres having improved fire resistance, it is generally desired to increase the amount of FeO, which preferably is then at least 6%, for instance up to 8% or higher, for instance 10%, and the MgO should then be at least 8%.

20 The analysis of the composition is preferably such that the fibres have a dissolution rate at pH 4.5 of at least 25, and preferably at least 40, nm per day. It is desirable for the dissolution rate to be as high as possible (consistent with retention of adequate humidity and heat resistance properties) but it is generally unnecessary for it to be above 150 or 100nm per day and it 25 is usually below 80nm per day.

30 Although a high dissolution rate at pH 7.5 has been proposed as a desirable property (as an indication of alleged biodegradability), in fact it is often an undesirable property since it is an indication of poor weathering resistance when exposed to humidity. Dissolution in the lungs at pH 7.5 is not exclusively necessary for the fibres to be biodegradable. Preferably the fibres have a dissolution rate in Gambles solution at pH 7.5 of below 25, and most preferably below 15, nm per 35 day.

The viscosity of the composition at 1400°C is usually at least 12 or 15 poise and is preferably at least 18

poise. Although it can be as high as, for instance, 60 poise it is generally below 40 poise and preferably it is not more than 30 poise.

When it is desired that the fibres should have good
5 fire resistance, the analysis is preferably such that the sintering temperature is at least 800°C and preferably at least 1,000°C.

The liquidus temperature is usually at least 1200°C
10 but often at least 1240°C. It can be as high as, for instance, 1400°C but preferably it is not more than 1340°C.

An advantage of the use of the moderate aluminium
melts defined for use in the invention is that it permits
the inclusion in the composition of readily available
15 materials having a moderate aluminium content such as rock,
sand and waste. This therefore minimises the need to use
expensive, high alumina materials such as bauxite or
kaolin, and minimises at the same time the need to use
expensive very low alumina materials such as silica sand or
20 olivine sand, iron ore, etc. These more expensive
materials may however be useful if desired. Typical,
readily available, medium alumina materials that may be
used as part or all of the composition include anorthosite
and phonolite and gabbros.

The composition is typically formed by blending
25 appropriate amounts of naturally occurring rock and sand
materials such as anorthosite, gabbros, limestone,
dolomite, diabase, apatite, boron-containing materials, and
waste materials such as mineral wool waste, alumina
silicates, slag, in particular high alumina (20-30%) slags
30 such as ladle slag, foundry sand, filter dust, fly ash,
bottom ash and high alumina waste from the production of
refractory materials.

The composition can be converted to a melt in
conventional manner, for instance in a gas heated furnace
35 or in an electric furnace or in a cupola furnace. An
advantage of the invention is that the composition can
easily have a reasonably low liquidus temperature (while

maintaining adequate viscosity at 1400°C) and this minimises the amount of energy that is required for forming the melt.

The melt can be converted to fibres in conventional manner, for instance by a spinning cup process or by a cascade rotor process, for instance as described in WO92/06047.

The fibres of the invention can have any convenient fibre diameter and length.

In this invention, dissolution rate is determined using the following test protocol.

300mg of fibres are placed in polyethylene bottles containing 500ml of a modified Gamble's solution (i.e., with complexing agents), adjusted to pH 7.5 or 4.5, respectively. Once a day the pH is checked and if necessary adjusted by means of HCl.

The tests are carried out during a one week period. The bottles are kept in water bath at 37°C and shaken vigorously twice a day. Aliquots of the solution are taken out after one and four days and analysed for Si on a Perkin-Elmer Atomic Absorption Spectrophotometer.

The modified Gamble's solution has the following composition:

	<u>g/l</u>	
25	MgCl ₂ .6H ₂ O	0.212
	NaCl	7.120
	CaCl ₂ .2H ₂ O	0.029
	Na ₂ SO ₄	0.079
	Na ₂ HPO ₄	0.148
30	NaHCO ₃	1.950
	(Na ₂ -tartrate).2H ₂ O	0.180
	(Na ₃ -citrate).2H ₂ O	0.152
	90% lactic acid	0.156
	Glycine	0.118
35	Na-pyruvate	0.172
	Formalin	1 ml

The fibre diameter distribution is determined for each sample by measuring the diameter of at least 200 individual fibres by means of the intercept method and a scanning electron microscope or optical microscope (1000 x magnification). The readings are used for calculating the specific surface of the fibre samples, taking into account the density of the fibres.

Based on the dissolution of SiO_2 (network dissolution), the specific thickness dissolved was calculated and the rate of dissolution established (nm/day). The calculations are based on the SiO_2 content in the fibres, the specific surface and the dissolved amount of Si.

In this specification, the sintering temperature is determined by the following test protocol.

A sample (5 x 5 x 7.5 cm) of mineral wool made of the fibre composition to be tested is placed in a furnace pre-heated to 700°C. After 1.5 hours exposure the shrinkage and the sintering of the sample were evaluated. The method is repeated each time with a fresh sample and a furnace temperature 50°C above the previous furnace temperature until the maximum furnace temperature, at which no sintering or no excessive shrinkage of the sample is observed, was determined.

In this specification, the viscosity in poise at 1400°C is calculated according to Bottinga and Weill, American Journal of Science Volume 272, May 1972, page 455-475.

The following are examples of the invention.

Compositions were formed by blending appropriate proportions of raw materials as shown in the table and each was melted in a crucible furnace and was fiberised by the cascade spinner technique. The melt viscosity and solubility of each was determined. The analyses of the compositions and their properties are quoted in the following tables. In the invention, any of compositions A to X are judged to be suitable and are selected for the

13

subsequent manufacture of MMVF products which are labelled as having good biological solubility. Those having viscosity above 20 and pH 4.5 solubility above 30 are preferred.

5 Product 1 is similar to, commercial slag wool and gives a poor viscosity. Product 2 is a high aluminium product but the proportions of all the components are such that the melt viscosity is too high for convenient spinning. Product 3 is similar to a conventional rock wool
10 product with normal good product properties but has a very low dissolution rate at pH 4.5. Accordingly products 1, 2 and 3 are not selected for use in the manufacture of biologically soluble MMV fibre products.

Fibre Types	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O	SUM	Vib pulse 1400°C	Diss rate pH 7.5 (st) nm/day	Diss rate pH 4.5 (st) nm/day	Sintering temp °C
5	A	34.5	28.0	1.8	3.3	25.4	5.6	0.6	100.0	21.2	9.5	34.8	>800
	B	36.2	26.3	1.9	4.9	17.7	10.8	1.0	100.0	19.4	6.8	45.1	>800
	C	38.3	25.0	1.7	3.0	24.9	5.6	0.7	100.0	24.7	7.4	53.8	>800
	D	38.1	24.7	1.8	4.6	17.4	11.3	1.2	100.0	20.0	7.9	64.2	>800
	E	43.2	20.0	1.6	5.0	16.6	11.5	1.2	100.0	22.8	5.0	57.9	>800
10	F	43.2	19.8	1.5	3.4	24.7	5.6	1.0	100.0	27.1	4.8	47.0	>800
	G	47.7	19.4	0.8	3.7	16.6	10.8	0.4	100.0	34.7	3.0	21.0	>800
	H	43.7	18.8	3.6	5.4	16.4	9.7	1.8	100.0	25.1	5.8	38.6	>800
	I	45.6	18.1	1.5	5.3	16.5	9.7	2.5	100.0	30.8	3.1	44.4	>800
	J	46.9	18.9	0.5	3.3	17.0	9.5	3.4	100.0	44.0	0.9	35.2	>800
15	K	44.1	18.7	1.6	5.2	16.5	9.8	3.3	100.0	30.3	2.6	41.1	>800
	L	39.6	24.3	1.8	3.2	21.7	6.7	1.8	100.0	30.8	5.7	49	>800
	M	43.8	20.4	1.2	10.3	15.6	8.3	0.2	100.0	21.9	3.9	39.7	>1000
	N	42.9	23.2	0.7	8.8	17.5	5.1	0.6	100.0	36.8	-	45.9	>900
	O	43.1	19.9	1.6	10.1	15.0	9.3	0.6	100.0	19.8	4.6	51.9	>1000
20	P	37.8	18.3	0.9	12.0	15.8	10.1	4.7	100.0	15.0	10.2	61.5	>1000
	Q	40.0	22.2	2.0	7.5	15.2	10.7	1.5	100.0	19.4	7.1	61.1	>1000
	R	45.4	14.5	1.6	5.6	15.3	7.2	9.0	100.0	39.9	3.1	48.1	>1000
	S	45.3	17.5	1.1	5.7	20.3	7.8	1.7	100.0	25.9	1.8	48.6	>1000
	T	43.1	14.0	0.7	0.5	34.3	5.2	0.7	100.0	15.2	1.5	59.8	>700
25	U	37.2	16.1	1.6	3.3	21.5	10.1	9.3	100.0	29.2	5.2	48.0	>800
	V	42.9	16.6	1.7	6.4	16.8	9.6	5.2	100.0	25.3	3.1	21.9	>1000
	W	38.9	16.4	1.4	8.4	20.0	7.9	6.4	100.0	20.2	9.5	33.0	>1000
	X	42.5	16.4	1.7	5.8	21.1	6.3	5.4	100.0	27.1	4.1	32.9	>1000
	Y	42.7	8.8	0.3	0.4	36.9	9.4	0.7	100.0	8.2	13.9	41.1	>700
30	Z	39.7	32.8	1.7	7.0	15.7	2.1	0.3	100.0	100.0	7.8	59.3	>1000
	1	46.9	13.2	3.0	6.4	17.1	9.4	2.6	100.0	23.7	2.0	3.0	>1000
	2												

The selected fibres may be provided in any of the forms conventional for MMV fibres. Thus they may be provided as a product consisting of loose, unbonded fibres.

More usually they are provided with a bonding agent, for 5 instance as a result of forming the fibres and connecting them in conventional manner. Generally the product is consolidated as a slab, sheet or other shaped article.

Products according to the invention may be formulated for any of the conventional purposes of MMV fibres, for 10 instance as slabs, sheets, tubes or other shaped products that are to serve as thermal insulation, fire insulation and protection or noise reduction and regulation, or in appropriate shapes for use as horticultural growing media, or as free fibres for reinforcement of cement, plastics or 15 other products or as a filler.

CLAIMS

1. A method of making man-made vitreous fibre products comprising forming one or more mineral melts and forming fibres from the or each melt characterised in that

5 the melt viscosity and the fibre dissolution rate at a pH in the range 4-5 are determined for the or each composition,

a composition is selected which has a viscosity at 1400°C of 10 to 70 poise and provides fibres which have a 10 dissolution rate of at least 20nm per day when measured at a pH of 4.5, and which includes, by weight of oxides,

	SiO ₂	32 to 48%
	Al ₂ O ₃	10 to 30%
	CaO	10 to 30%
15	MgO	2 to 20%
	FeO	2 to 15%
	Na ₂ O + K ₂ O	0 to 12%
	TiO ₂	0 to 6%
	Other Elements	0 to 15%

20 and the selected composition is utilised for making the man-made vitreous fibres.

2. Use as biologically acceptable man-made vitreous fibres of fibres formed of a composition which includes, by weight of oxides,

25	SiO ₂	32 to 48%
	Al ₂ O ₃	10 to 30%
	CaO	10 to 30%
	MgO	2 to 20%
	FeO	2 to 15%
30	Na ₂ O + K ₂ O	0 to 12%
	TiO ₂	0 to 6%
	Other Elements	0 to 15%

and the composition has a viscosity at 1400°C of 10 to 70 poise,

35 and the fibres have a dissolution rate of at least 20nm per day when measured at a pH of 4.5.

3. A package containing a man-made vitreous fibre product wherein the fibres are formed of a composition having an analysis, as oxides, which includes

	SiO ₂	32 to 48%
5	Al ₂ O ₃	10 to 30%
	CaO	10 to 30%
	MgO	2 to 20%
	FeO	2 to 15%
	Na ₂ O + K ₂ O	0 to 12%
10	TiO ₂	0 to 6%
	Other Elements	0 to 15%

and the composition has a viscosity at 1400°C of 10 to 70 poise,

15 and the fibres have a dissolution rate at pH 4.5 of at least 20nm per day,

and the package includes a label or insert, or is associated with advertising, referring to solubility at pH 4 to 5 and/or in environment created by macrophages in lung fluid.

20 4. The invention according to any preceding claim in which the dissolution rate at pH 4.5 is 25 to 100nm, preferably 40 to 80nm, per day.

5. The invention according to any preceding claim in which the composition has a viscosity of 18 to 40 poise at 25 1400°C.

6. The invention according to any preceding claim in which the fibres have a dissolution rate at pH 7.5 below 15nm per day.

7. The invention according to any preceding claim in 30 which the fibres have a sintering temperature of at least 800°C, preferably at least 1000°C.

8. The invention according to any preceding claim in which the composition provides a liquidus temperature of 1240 to 1340°C.

35 9. The invention according to any preceding claim in which Na₂O+K₂O is not more than 10%.

10. The invention according to any preceding claim in which Al_2O_3 is 18-30%, $\text{SiO}_2+\text{Al}_2\text{O}_3$ is 60-75%, FeO is 2-12%, $\text{Na}_2\text{O}+\text{K}_2\text{O}$ is 0-7%, TiO_2 is 0-4% and other elements is 0-8%.

11. The invention of any of claims 1 to 9 in which the 5 amount of Al_2O_3 is below 19%.

12. A product comprising man-made vitreous fibres formed of a composition having an analysis, as oxides, which includes

	SiO_2	32 to 48%
10	Al_2O_3	10 to 18%
	CaO	10 to 30%
	MgO	2 to 20%
	FeO	2 to 15%
	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	6 to 12%
15	TiO_2	0 to 6%
	Other Elements	0 to 15%

and the composition has a viscosity at 1400°C of 10 to 70 poise,

20 and the fibres have a dissolution rate at pH 4.5 of at least 20nm per day.

13. The invention of claim 12 in which Al_2O_3 is 13 to 18% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is at least 6%.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :		(11) International Publication Number:	WO 96/14274
C03C 13/00		A3	(43) International Publication Date: 17 May 1996 (17.05.96)
(21) International Application Number: PCT/EP95/04394		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).	
(22) International Filing Date: 8 November 1995 (08.11.95)			
(30) Priority Data:			
9422468.0	8 November 1994 (08.11.94)	GB	
9424126.2	23 November 1994 (23.11.94)	GB	
9424127.2	23 November 1994 (23.11.94)	GB	
9500667.2	13 January 1995 (13.01.95)	GB	
(71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S. [DK/DK]; Hovedgaden 501, DK-2640 Hedehusene (DK).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): JENSEN, Soren, Lund [DK/DK]; Tordenskjoldsgade 23, 2 th., DK-1055 Kobenhavn (DK). CHRISTENSEN, Vermund, Rust [DK/DK]; Soager 11, DK-4000 Roskilde (DK). GULDBERG, Marianne [DK/DK]; Niels Finsens Alle 5, DK-2860 Soborg (DK).			
(74) Agent: JONES, Helen; Gill Jennings & Every, Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).			

(54) Title: MAN-MADE VITREOUS FIBRES

(57) Abstract

Man-made vitreous fibres have a solubility at pH 4.5 of at least 20 nm per day and a melt viscosity of 10-70 poise at 1,400 °C. A composition which will provide these properties is selected for their manufacture and contains at least 10 % by weight Al₂O₃. Novel fibres contain at least 6 % by weight Na₂O + K₂O.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INTERNATIONAL SEARCH REPORT

Intern'l Application No
PCT/EP 95/04394A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 662 687 (ISOVER SAINT-GOBAIN) 16 December 1991 see page 5, line 25 - line 34; claims; examples; tables I,II ---	1-12
X	EP,A,0 459 897 (ISOVER SAINT-GOBAIN) 4 December 1991 see claims; examples see the whole document ---	1-4
A	EP,A,0 231 691 (ISOVER SAINT-COBAIN) 12 August 1987 see the whole document ---	5-12
A	EP,A,0 231 691 (ISOVER SAINT-COBAIN) 12 August 1987 see the whole document ---	1-12
A	GB,A,2 152 026 (INSTITUT FUER MINERALISCHE-UND LAGERSTATTENWIRTSCHAFT DRESDEN) 31 July 1985 see the whole document -----	1-12

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

1

Date of the actual completion of the international search

23 May 1996

Date of mailing of the international search report

07.06.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentdaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 cpo nl.
 Fax (+ 31-70) 340-3016

Authorized officer

Harbron, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 95/04394

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2662687	06-12-91	NONE		
EP-A-459897	04-12-91	FR-A- 2662688 AT-T- 121378 AU-B- 642493 AU-B- 7731891 CA-A- 2043699 CN-A- 1059135 DE-D- 69108981 DE-T- 69108981 ES-T- 2073136 HU-B- 212280 JP-A- 4228455 PL-B- 167825 US-A- 5250488		06-12-91 15-05-95 21-10-93 05-12-91 02-12-91 04-03-92 24-05-95 07-12-95 01-08-95 29-04-96 18-08-92 30-11-95 05-10-93
EP-A-231691	12-08-87	FR-A- 2591423 DE-A- 3684695 JP-A- 62148337 US-A- 5037470 US-A- 4867779		19-06-87 07-05-92 02-07-87 06-08-91 19-09-89
GB-A-2152026	31-07-85	DE-A- 3438733 SE-A- 8406571		11-07-85 01-07-85